AD-A148 826 MARINE EXPOSURE OF PRESERVATIVE-TREATED SMALL WOOD PANELS(U) FOREST PRODUCTS LAB MADISON WI B R JOHNSON ET AL. OCT 84 FSRN-FPL-0248 1/1

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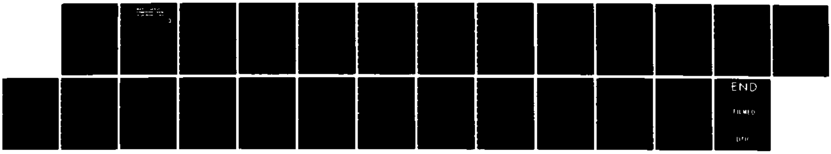

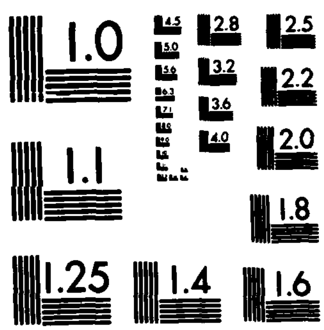

MICROCOPY RESOLUTION TEST CHART
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United States Department of Agriculture

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Research Note FPL-0248

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Marine Exposure of Preservative-Treated Small Wood Panels

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Abstract

Small wood panels treated with many different chemicals have been exposed to limnorian and teredine marine borers in the sea at Key West, Florida. These preservatives and treatments include creosotes with and without modification, waterborne salts, salt-creosote dual treatments, chemical modifications of wood, and modified polymers. In spite of the accelerated nature of this test, many treated panels remain free of attack after 13-1/2 years in the sea. Untreated panels have been badly damaged by marine borers in 6 to 18 months. Borer activity has lessened in recent years.

Keywords: Wood preservation, marine borers, creosote, *Limnoria*, teredines, CCA, durability.

Introduction

The effectiveness of conventional preservatives in preventing biodegradation of wood above ground, in soil contact, and in fresh-water exposures is well documented. However, these preservatives may be much less effective in the marine environment. This is especially true in warmer waters where the crustacean borer *Limnoria tripunctata* L. is prevalent. This organism readily attacks creosote-treated wood. Because of observations that metallic salts deter *L. tripunctata* and that creosote impedes attack by teredine borers, we began an accelerated test in 1969 to determine which commercially available formulation(s) of these preservatives would afford maximum protection where

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The Laboratory is maintained in cooperation with the University of Wisconsin.

The paper supercedes Research Paper FPL 399 of the same title, published in 1981.

L. tripunctata and teredine borers are abundant. Since then, as promising new or candidate preservatives have appeared, we have installed additional test specimens in hopes of finding still simpler, lower cost, or more effective treatments. This report compares the effectiveness of 250 preservative treatments in protecting small wood panels from teredines and *Limnoria* for up to 13.5 years. A number of treatments not included in the first report of this work (Johnson and Gutzmer 1981) or earlier publications on the original study (Johnson et al. 1973; Johnson 1977; Johnson 1982) are included here.

Procedures

With few exceptions, we have followed American Society for Testing and Materials Standard D 2481 (ASTM 1981). Preparation of test specimens entailed:

1. Selecting southern pine sapwood with 6 to 9 rings per inch.
2. Machining into vertical-grain panels 0.6 x 3.8 x 15.2 cm (1/4 x 1-1/2 x 6 in.).
3. Pressure treating with preservative to calculated gain-in-weight retentions.
4. Destructive chemical analysis of some specimens to determine retentions.
5. Installing five replicates per treatment (except where noted differently) at test site.

From December 1969 to January 1979, panels were exposed under Pier No. 1 of the Key West Naval Station (now Truman Annex), Key West, Florida. In 1979 we had to move all test materials to another Key West harbor at the Trumbo Annex. At both harbors, panels were suspended on fiberglass racks 1 to 2 feet below the low-tide level. Both harbors have active populations of *L. tripunctata* and teredines; the Trumbo Annex area has somewhat more teredine and less *Limnoria* activity than did the Truman site. We have not observed attack on panels by pholad or *Sphaeroma* borers at either site.

Although the ASTM standard calls for monthly inspections of test panels of this size, inspections made at semiannual intervals seemed adequate. In 1973 and 1974, we inspected only once each year. At each inspection, we scraped all panels free of fouling and rated them for the type and extent of marine-borer attack. We visually rated the panels as follows:

Rating	Extent of Attack
10	No more than trace
9	Light
7	Moderate
4	Heavy
0	Complete destruction

Untreated control panels installed at each inspection have provided checks on borer activity.

Preservatives and preservative processes tested and reported here are indexed in table 1. The Forest Products Laboratory (FPL) did nearly all the treatments. Further information on preservative composition and treating data is generally available from the FPL contact given in table footnotes.

Relevant federal specifications and American Wood-Preservers' Association (AWPA) standards are given where available. Retentions are by gain in weight in pounds per cubic foot (pcf). Retentions of waterborne salts are expressed on an oxide basis.

Discussion of Results

The performance of most panels in marine exposure is presented as present (July 1983) (average) condition, total years of exposure, and years of exposure until the average rating dropped below 6 (tables 2-1 through 2-7 and 3-4 through 6-3). Tables 3-1, 3-2, and 3-3 for chromated copper arsenate Types B and C, and ammoniacal copper arsenate, respectively, give individual panel ratings rather than an average condition because of extensive microbial damage to some panels and the commercial importance of these three preservatives. *This microbial damage, apparently by soft-rot fungi, results in* a slow surface erosion. The erosion probably would be of little significance except for the thinness (1/4 in.) of the test panels. The erosion is noted because it has, in some cases, interfered with the objective of evaluating resistance to marine borers. Comparisons between preservative treatments should be made on the basis of marine-borer damage, not microbial erosion.

The column showing years of exposure until the average rating fell below 6 (or individual rating below 7) will be the most useful for comparisons of preservative effectiveness. Once attack has progressed to this point, it usually continues steadily to destruction of the test panel. The numerical rating only reflects marine-borer attack, not microbial erosion. A condition of E alone denotes total failure due to erosion by microorganisms. Where failure of a treatment group was attributed to both borers and microbes, but some panels within the group failed by erosion alone, that proportion is footnoted in the tables. Retention should be considered in any comparisons of preservative effectiveness.

Marine-borer activity has fluctuated over the years, as is evidenced by control panel ratings (fig. 1). Borer activity dropped off some beginning in 1975 and declined further when panels were moved to the new site in 1979. Hence, where two preservatives under comparison may have been exposed at different times, the performance of untreated (control) panels during these times should be considered. Generally, controls fell below a mean rating of 6 in 6 to 12 months.

This marine-exposure test measures relative effectiveness of preservatives in small sawn specimens at one exposure site. The presence of other types of marine borers at other sites could result in very different performance. Extrapolation of our results to piling is questionable on several counts: These panels provide an accelerated test because they expose more of the earlywood preferred by *Limnoria* than do pilings; the greater surface-to-volume ratio of small panels permits faster loss of preservative; the cross section of our panels is small enough that *Limnoria* can penetrate deeply and still obtain good exchange of oxygenated water, whereas in piling, wave action and abrasion from floating debris must break away surface areas before *Limnoria* can burrow more deeply.

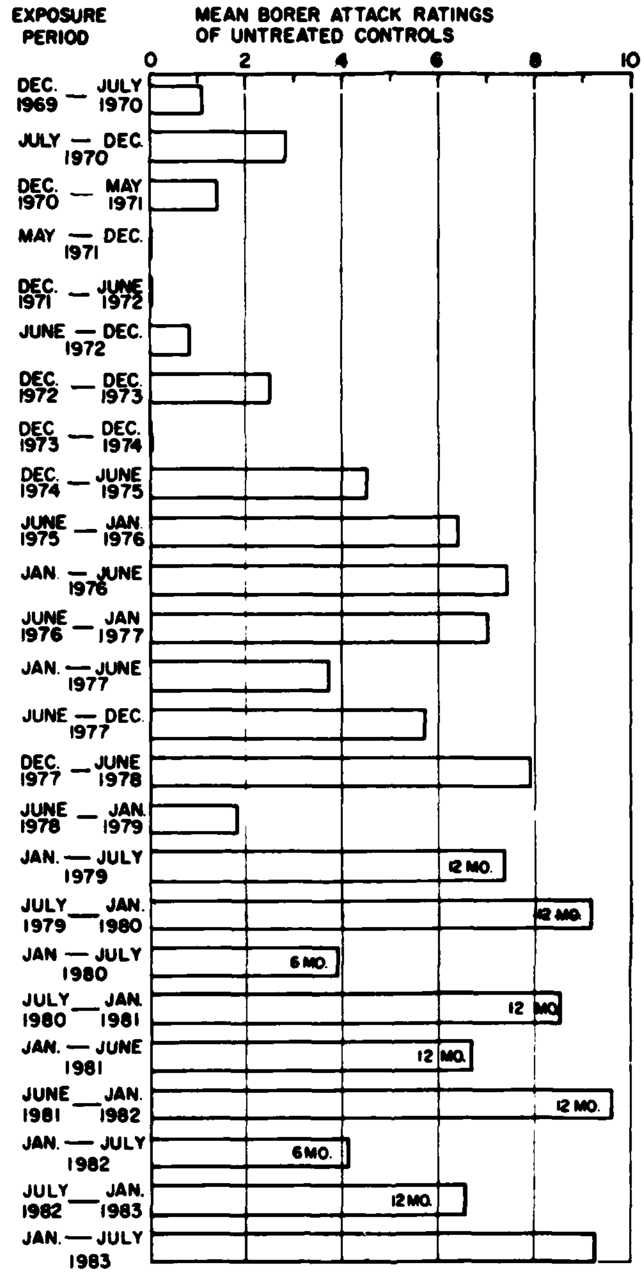

Figure 1.—Ten to twenty-five control panels were installed every 6 months to monitor marine-borer activity. The average condition of these panels 6 months after installation varied from nearly sound to destroyed, as represented by the bar values. Values within the bars, from January 1979 on, represent the number of months of exposure until this set of controls reached an average rating below 6, representing moderate to heavy borer damage. (ML84 5292)

Conclusions

Creosotes

Vertical-retort creosote (table 2-1), probably because of its low aromaticity, compares poorly with both land (table 2-2) and marine (table 2-3) grades. Performance of the land and marine creosotes was improved by increasing retentions. Increasing the concentration of the creosote components anthracene, phenanthrene, carbazole, and naphthalene (tables 2-4, 2-5, 2-6) has had little effect on performance of marine-grade coal-tar creosote.

Waterborne Salts

Chromated copper arsenate (CCA) Type B (table 3-1) and Type C (table 3-2) have protected the wood panels about equally well. Prior to erosion failure, ammoniacal copper arsenate (ACA) (table 3-3) deterred borers as well as CCA. Both CCA types resisted borers about as well at 1.1 pcf as at 2.3 pcf, until microbial erosion eliminated the 1.1 pcf panels after about 11 years. At 1.1 and 2.5 pcf, both types of CCA protected against *Limnoria tripunctata* better than high retentions of marine creosote. With 7-1/2 years' exposure, acid copper chromate (ACC) (table 3-4), ammoniacal copper borate (ACB) (table 3-5), and ammoniacal copper fluoride (ACF) (table 3-7) have performed similarly to CCA at 0.6 pcf. However, the 0.6 pcf CCA panels were exposed longer at the more severe original site. These other treatments were exposed for only 3 years at Truman Annex before all specimens were moved to Trumbo Point. Microbial destruction of ACA panels prevents a comparison with that formulation. Copper salts of tetra- and pentachlorophenol (table 3-9) were not effective against *Limnoria* or teredines.

Dual Treatments

With treatments of CCA (tables 4-1, 4-4) or ACA (table 4-7) followed by vertical-retort creosote, increasing the salts retention improved performance but increasing the creosote retention did not. Subsequent treatment of CCA-treated panels with either land (tables 4-2, 4-5) or marine (tables 4-3, 4-6) creosote improved performance over that obtained with CCA and vertical-retort creosote treatment (tables 4-1, 4-4). CCA types B and C have performed about equally well in dual treatments. ACA (table 4-9) in dual treatments seems to be slightly more effective than ACB (table 4-10). The waterbornes ACC (table 4-11) and CCF (table 4-12) so far have performed similarly to CCA (tables 4-3, 4-6) in dual treatments.

Modified Wood and Polymers

Chemical modification of panels with propylene oxide (table 5) has prevented attack by *Limnoria* and teredines for 8 years. Panels treated with butylene oxide (table 5) are unattacked after 5-l/2 years. Impregnation with tributyltin (TBT) oxide (table 6-1), TBT-modified methacrylate polymers (table 6-1), or TBT-modified monomers (with subsequent polymerization) (tables 6-2, 6-3) has prevented borer damage for 6 to 6-1/2 years. Methacrylates modified with pentachlorophenol or pentabromophenol have deterred borers for 3-1/2 years to date (table 6-3).

This marine-exposure test will continue and promising candidate preservatives may be added. We will publish a new edition of this report when enough significant new data accumulate to warrant it.

Acknowledgments

Financial support from the Naval Facilities Engineering Command, U.S. Navy, for a portion of this research, is gratefully acknowledged. Several chemical and wood preserving companies have contributed to this work. These firms are identified in footnotes to the relevant tables. Particular thanks are due Daniel Probert and staff of the Naval Air Development Center, Anti-Submarine Warfare Field Station, Trumbo Annex, Key West, Florida, for use of the exposure site and help with inspections.

Literature Cited

American Society for Testing and Materials. Standard method of accelerated evaluation of wood preservatives for marine services by means of small-size specimens. ASTM Stand. Desig. D 2481-70. Philadelphia, PA: American Society for Testing and Materials; 1981.

Johnson, B. R.; Gjovik, L. R.; Roth, H. G. Single- and dual-treated panels in a semi-tropical harbor: Preservative and retention variables and performance. Am. Wood-Preservers' Assoc. Proc. 69: 207-215; 1973.

Johnson, B. R. Performance of single- and dual-treated panels in a semi-tropical harbor. Progress Report No. 2. Am. Wood-Preservers' Assoc. Proc. 73: 174-177; 1977.

Johnson, B. R. A look at creosote vs. chromated copper arsenate salts as wood preservatives for the marine environment. Ind. Eng. Chem. Prod. Res. Dev. 21(4): 704-705; 1982.

Johnson, B. R.; Gutzmer, D. I. Marine exposure of preservative-treated small wood panels. Res. Pap. FPL 399. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory; 1981.

Table 1.—Index to treatments tested and tabular data of their performance

Treatment	Table No.	Treatment	Table No.
Creosotes		Chromated copper arsenate (C) and land-grade coal-tar creosote	4-5
English vertical retort	2-1	Chromated copper arsenate (C) and marine-grade coal-tar creosote	4-6
Coal-tar, land and fresh-water grade	2-2	Ammoniacal copper arsenate and English vertical-retort creosote	4-7
Coal-tar, marine grade	2-3	Ammoniacal copper arsenate and land-grade coal-tar creosote	4-8
Coal-tar, with supplements	2-4	Ammoniacal copper arsenate and marine-grade coal-tar creosote	4-9
Coal-tar, with supplemental naphthalene	2-5	Ammoniacal copper borate and marine-grade coal-tar creosote	4-10
Coal-tar solution, alone and with supplements	2-6	Acid copper chromate and marine-grade coal-tar creosote	4-11
Coal-tar, with supplemental Endrin	2-7	Chromated copper fluoride and marine-grade coal-tar creosote	4-12
Waterborne salts		Chemical modification	5
Chromated copper arsenate (B)	3-1	**Polymers**	
Chromated copper arsenate (C)	3-2	Prepolymerized tributyltin methacrylate and methyl methacrylate copolymers	6-1
Ammoniacal copper arsenate	3-3	*In situ* polymerization of tributyltin-modified monomers	6-2
Acid copper chromate	3-4	*In situ* polymerization of modified methacrylate impregnants	6-3
Ammoniacal copper borate	3-5		
Double diffusion	3-6		
Ammoniacal copper fluoride	3-7		
Chromated copper fluoride	3-8		
Copper tetra- and pentachlorophenol	3-9		
Ammoniacal copper zinc arsenate	3-10		
Dual treatments			
Chromated copper arsenate (B) and English vertical-retort creosote	4-1		
Chromated copper arsenate (B) and land-grade coal-tar creosote	4-2		
Chromated copper arsenate (B) and marine-grade coal-tar creosote	4-3		
Chromated copper arsenate (C) and English vertical-retort creosote	4-4		

CREOSOTES

Table 2-1.—English vertical-retort creosote[1]

Retention	Installation date	Present condition[2]	Total exposure	Exposure until average rating <6
Pcf			*Years*	*Years*
9.7	12/69	L	1-1/2	1
14	12/69	L	1-1/2	1
27	12/69	L	2-1/2	2
28	7/82	10	1	—
[3]20	7/82	10	1	—

[1]Study supported in part by the U.S. Navy Naval Facilities Engineering Command (NFEC). FPL contact, B. R. Johnson.

[2]L = destroyed by *Limnoria*.

[3]Solution of 2% diflubenzuron, 48% dimethyl sulfoxide, 50% vertical-retort creosote.

Table 2-2.—Coal-tar creosote, land and fresh-water grade (AWPA P-1, Federal Specification TT-C-645)[1]

Retention	Installation date	Present condition[2]	Total exposure	Exposure until average rating <6
Pcf			*Years*	*Years*
6.6	12/69	L	2	1
16	12/69	L	3	2
24	12/69	L	13	3

[1]Study supported in part by NFEC. FPL contact, B. R. Johnson.

[2]L = destroyed by *Limnoria*.

Table 2-3.—Coal-tar creosote, marine grade (AWPA P-13, Federal Specification TT-C-645)[1]

Retention	Installation date	Present condition[2]	Total exposure	Exposure until average rating <6
Pcf			*Years*	*Years*
6.5	12/69	L	2	1
15	12/69	L	4	2
28	12/69	L	5-1/2	4
39	12/70	1	12-1/2	11
15	1/76	L	6	3-1/2
[3]20	1/77	L	2-1/2	3-1/2

[1]Study supported in part by NFEC, Koppers Co. Organic Materials Division (OMD), and J. H. Baxter and Co. FPL contact, B. R. Johnson.

[2]L = destroyed by *Limnoria*.

[3]Based on 10 replicates.

Table 2-4.—Coal-tar creosote (AWPA P-13, Federal Specification TT-C-645) with supplements[1,2]

Preservative supplement	Retention	Installation date	Present condition[3]	Total exposure	Exposure until average rating <6
	Pcf			*Years*	*Years*
10 pct PAC[4]	20	6/76	L	5	2-1/2
10 pct PAC + 20 pct naphthalene	18	6/76	L	4	2-1/2
20 pct PAC + 20 pct naphthalene	19	6/76	L	4	3

[1]Study supported in part by Koppers Co. OMD. FPL contacts, L. R. Gjovik and B. R. Johnson.

[2]10 replicates per treatment.

[3]L = destroyed by *Limnoria*.

[4]PAC = A fraction of creosote containing a high percentage of crystals, primarily of phenanthrene, anthracene, and carbazole.

Table 2-5.—Coal-tar creosote (AWPA P-13, Federal Specification TT-C-645) with supplemental naphthalene[1,2]

Preservative supplement (naphthalene)	Retention	Installation date	Present condition[3]	Total exposure	Exposure until average rating <6
	Pcf			*Years*	
11 pct	[4]19	6/75	L	6-1/2	3-1/2
	36	12/77	10	5-1/2	—
20 pct	[4]17	6/75	L	6	2-1/2
	22	6/76	L	3-1/2	2-1/2
	34	12/77	9	5-1/2	—
30 pct	[4]19	6/75	L	6	4
	22	6/76	L	5	2-1/2
	31	12/77	7	5-1/2	—
40 pct	38	12/70	5	12-1/2	11-1/2
	[4]18	6/75	L	5	3
	18	6/76	L	4	2-1/2
	38	12/77	8	5-1/2	—

[1]Study supported in part by Koppers Co. OMD. FPL contact, B. R. Johnson.

[2]10 replicates per treatment except 12/70 installation with 5 replicates.

[3]L = destroyed by *Limnoria*.

[4]Full-cell treatments with toluene dilution of the creosote.

Table 2-6.—Creosote/coal-tar solution alone and with supplements (AWPA P-13, Federal Specification TT-C-645)[1,2]

Preservative supplement	Retention	Installation date	Present condition	Total exposure	Exposure until average rating <6
	Pcf			*Years*	
None	35.0	7/79	8	4	—
6 pct sulfur + 20 pct naphthalene	32.8	7/79	5	4	3-1/2
6 pct tar bases + 20 pct naphthalene	33.9	7/79	8	4	—
11 pct tar bases + 20 pct naphthalene	30.7	7/79	5	4	4

[1]Study in cooperation with and treatments performed by Koppers Co. OMD. FPL contact, B. R. Johnson.

[2]10 replicates per treatment.

Table 2-7.—Coal-tar creosote, land and fresh-water grade (AWPA P-1, Federal Specification TT-C-645) with supplemental Endrin[1,2]

Preservative supplement (Endrin)	Retention	Installation date	Present condition	Total exposure	Exposure until average rating <6
Pct	*Pcf*			*Years*	
None	10.1	1/83	10	1/2	—
None	37.6	1/83	10	1/2	—
0.1	11.0	1/83	10	1/2	—
.1	33.6	1/83	10	1/2	—
.2	10.4	1/83	10	1/2	—
.2	30.9	1/83	10	1/2	—
.4	9.9	1/83	10	1/2	—
.4	35.2	1/83	10	1/2	—

[1]Study in cooperation with Koppers Co. OMD. FPL contact, B. R. Johnson.

[2]10 replicates per treatment.

WATERBORNE SALTS

Table 3-1.—Chromated copper arsenate (AWPA P-5 Type B, Federal Specification TT-W-550 Type II)[1,2]

Retention	Installation date	Present condition[3]	Total exposure	Exposure until rating <7
Pcf			*Years*	
0.23	12/69	L	2	2
.23	12/69	L,T	2-1/2	2-1/2
.23	12/69	L	2-1/2	2-1/2
.23	12/69	L	2-1/2	2
.23	12/69	L,T	2-1/2	2
.58	12/69	T	3	3
.56	12/69	L	5-1/2	5
.58	12/69	L	5	5
.57	12/69	L	6-1/2	6-1/2
1.1	12/69	E	10-1/2	—
1.1	12/69	L,E	10-1/2	—
1.1	12/69	E	11	—
1.1	12/69	10	13-1/2	—
2.3	12/69	10	13-1/2	—
2.3	12/69	([4])	—	—

[1]Study supported in part by NFEC. FPL contact, B. R. Johnson.

[2]Data are for individual panels.

[3]L, T, E = destroyed by *Limnoria*, teredines, microbial erosion, respectively.

[4]Lost when sound at 7-1/2 years.

Table 3-2.—Chromated copper arsenate (AWPA P-5 Type C, Federal Specification TT-W-550 Type III)[1,2]

Retention	Installation date	Present condition[3]	Total exposure	Exposure until rating <7
Pcf			——— *Years* ———	
0.25	12/69	L,T	2-1/2	2
.25	12/69	L,T	3	3
.25	12/69	L	2-1/2	2-1/2
.26	12/69	L	2-1/2	2
.60	12/69	L,T	8-1/2	6-1/2
.60	12/69	L	5	5
.60	12/69	L,T	7	7
.59	12/69	L	6	6
1.1	12/69	E	11-1/2	—
1.1	12/69	E	11	—
1.1	12/69	L,E	11	—
2.3	12/69	10	13-1/2	—
2.4	12/69	10	13-1/2	—
2.4	12/69	10	13-1/2	—
2.4	12/69	10	13-1/2	—
2.4	12/69	10	13-1/2	—

[1]Study supported in part by NFEC. FPL contact, B. R. Johnson.

[2]Data are for individual panels.

[3]L, T, E = destroyed by *Limnoria*, teredines, microbial erosion.

Table 3-3.—Ammoniacal copper arsenate (AWPA P-5, Federal Specification TT-W-549)[1,2]

Retention	Installation date	Present condition[3]	Total exposure	Exposure until rating <7
Pcf			——— *Years* ———	
0.23	12/69	L	3	3
.24	12/69	L,T	2-1/2	2-1/2
.23	12/69	L,T	3	3
.23	12/69	L,T	3	3
.23	12/69	L	2-1/2	2
.55	12/69	E	6	—
.56	12/69	E	6	—
.56	12/69	E	6-1/2	—
.55	12/69	E	6	—
.56	12/69	E	6	—
1.1	12/69	E	9-1/2	—
1.1	12/69	E	9	—
.95	12/69	E	10-1/2	—
1.1	12/69	E	8-1/2	—
1.1	12/69	E	8-1/2	—
2.4	12/69	E	10	—
2.3	12/69	E	10-1/2	—

[1]Study supported in part by NFEC. FPL contact, B. R. Johnson.

[2]Data are for individual panels.

[3]L, T, E = destroyed by *Limnoria*, teredines, microbial erosion.

Table 3-4.—Acid copper chromate (AWPA P-5, Federal Specification TT-W-546)[1,2]

Retention	Installation date	Present condition[3]	Total exposure	Exposure until rating <6
Pcf			*Years*	*Years*
0.25	6/75	L,E	6	4-1/2
.25	1/76	2	7-1/2	3-1/2
.60	1/76	10	7-1/2	—
1.2	1/76	10	7-1/2	—
2.8	1/76	10	7-1/2	—

[1]*Study supported in part by Koppers Co., Forest Products Division (FPD).* FPL contact, L. R. Gjovik.

[2]15 replicates per treatment except 6/75 installation with 8 replicates.

[3]L, E = destroyed by *Limnoria*, microbial erosion.

Table 3-5.—Ammoniacal copper borate[1,2]

Retention	Installation date	Present condition[3]	Total exposure	Exposure until rating <6
Pcf			*Years*	*Years*
1.3	6/75	L,E[4]	5-1/2	4
.25	1/76	L,E[5]	6-1/2	3
.60	1/76	L,T,E[6]	7	6
1.2	1/76	10	7-1/2	—
2.5	1/76	10	7-1/2	—

[1]Study supported in part by J. H. Baxter and Co. FPL contact, B. R. Johnson.

[2]As $2CuO{\cdot}B_2O_3$. 15 replicates per treatment.

[3]L, T, E = destroyed by *Limnoria*, teredines, microbial erosion.

[4]1 of 5 panels failed solely from microbial erosion.

[5]2 of 15 panels failed solely from microbial erosion.

[6]8 of 15 panels failed solely from microbial erosion.

Table 3-6.—Double diffusion with sodium fluoride and copper-containing solutions[1,2]

Preservative formulation	Duration of treatment	Installation date	Present condition[3]	Total exposure	Exposure until average rating <6
	Hr			*Years*	*Years*
1.5% NaF	96				
+ 1.5% $CuSO_4$	138	6/75	5	8	7
1.5% NaF	96				
+ 1.5% ACC	138	6/75	L,T	5-1/2	4

[1]FPL contact, L. R. Gjovik.

[2]Samples saturated with water, soaked in NaF, then soaked in $CuSO_4$ or ACC. 8 replicates per treatment.

[3]L, T = destroyed by *Limnoria*, teredines.

Table 3-7.—Ammoniacal copper fluoride[1,2]

Preservative formulation (ratio)	Retention	Installation date	Present condition[3]	Total exposure	E a ra
	Pcf			——————— *Years* -	
CuO/F = 5.6	0.52	1/76	L,E[4]	7	
	.90	1/76	6	7-1/2	
CuO/F = 2.4	.62	1/76	5	7-1/2	
	1.3	1/76	10	7-1/2	
	2.4	1/76	10	7-1/2	
CuO/F = 1.2	.61	1/76	L,E[5]	6	
	1.2	1/76	10	7-1/2	
	2.6	1/76	10	7-1/2	

[1]Study supported in part by J. H. Baxter and Co. FPL contact, L. R. Gjovik.

[2]10 replicates per treatment.

[3]L, E = destroyed by *Limnoria*, microbial erosion.

[4]9 of 10 panels failed solely from microbial erosion.

[5]5 of 10 panels failed solely from microbial erosion.

Table 3-8.—Chromated copper fluoride[1]

Retention	Installation date	Present condition[2]	Total exposure	Ex ra
Pcf			———————— *Years* ——	
0.23	6/77	L,T	4	
.60	6/77	L	5	
1.2	6/77	10	6	
2.5	6/77	10	6	

[1]Study supported in part by Simonsen Chemical Co. FPL contact, L. R. Gjovik.

[2]L, T = destroyed by *Limnoria*, teredines.

Table 3-9.—Copper salts of tetrachlorophenol and pentachlorophenol[1]

Preservative formulation	Retention	Instal-lation date	Present condition[2]	Total exposure	Exposure until average rating <6
	Pcf			*Years*	*Years*
3.42 pct tetrachlorophenol + 0.58 pct CuO	1.7	6/78	L,T	4	2-1/2
0.855 pct tetrachlorophenol + 0.145 pct CuO	.36	6/78	L	3	2
3.42 pct tetrachlorophenol + 0.145 pct CuO	1.4	6/78	L,T,E[3]	4-1/2	3-1/2
0.855 pct tetrachlorophenol + 0.145 pct CuO	.28	6/78	L	2-1/2	2
3.42 pct pentachlorophenol + 0.58 pct CuO	1.5	6/78	L,E	5	3
0.855 pct pentachlorophenol + 0.145 pct CuO	.39	6/78	L	4-1/2	2-1/2

[1]Study supported in part by Reichhold Chemicals, Inc. FPL contact, B. R. Johnson.

[2]L, T, E = destroyed by *Limnoria*, teredines, microbial erosion.

[3]1 panel failed solely from microbial erosion.

Table 3-10.—Ammoniacal copper zinc arsenate[1,2]

Retention	Installation date	Present condition[3]	Total exposure	Exposure until rating <6
Pcf			*Years*	*Years*
0.25	7/82	10	1	—
.6	7/82	10	1	—
1.2	7/82	10	1	—
1.6	7/82	10	1	—
2.0	7/82	10	1	—
2.5	7/82	10	1	—

[1]Study supported in part by J. H. Baxter and Co. FPL contact, B. R. Johnson.

[2]10 replicates per treatment.

DUAL TREATMENT

Table 4-1.—Dual treatment with chromated copper arsenate (Type B) and English vertical-retort creosote[1]

Retention: Chromated copper arsenate	Retention: Creosote	Installation date	Present condition[2]	Total exposure	Exposure until average rating <6
———Pcf———				———Years———	
0.25	9.0	12/69	L,T	4	3
.23	16	12/69	L,T	6	5
.22	27	12/69	L	6-1/2	2-1/2
.59	7.9	12/69	L,E	12	10
.58	13	12/69	L,E	10-1/2	9
.58	30	12/69	L	10-1/2	8-1/2
1.1	8.1	12/69	10	13-1/2	—
1.1	11	12/69	9	13-1/2	—
1.1	25	12/69	5	13-1/2	13
2.4	9.0	12/69	10	13-1/2	—
2.3	16	12/69	10	13-1/2	—
2.4	24	12/69	10	13-1/2	—

[1]Study supported in part by NFEC. FPL contact, B. R. Johnson.

[2]L, T, E = destroyed by *Limnoria*, teredines, microbial erosion.

Table 4-2.—Dual treatment with chromated copper arsenate (Type B) and land-grade coal-tar creosote (P-1)[1]

Retention: Chromated copper arsenate	Retention: Creosote	Installation date	Present condition[2]	Total exposure	Exposure until average rating <6
———Pcf———				———Years———	
0.22	6.8	12/69	L	8-1/2	6
.23	14	12/69	L	9	8
.23	25	12/69	L	9	8-1/2
.57	7.1	12/69	L	10-1/2	9
.59	18	12/69	4	13-1/2	13
.59	18	12/69	5	13-1/2	13
1.1	5	12/69	10	13-1/2	—
1.1	16	12/69	10	13-1/2	—
1.1	18	12/69	9	13-1/2	—
2.3	5	12/69	10	13-1/2	—
2.4	16	12/69	10	13-1/2	—
2.3	21	12/69	10	13-1/2	—

[1]Study supported in part by NFEC. FPL contact, B. R. Johnson.

[2]L = destroyed by *Limnoria*.

Table 4-3.—Dual treatment with chromated copper arsenate (Type B) and marine-grade coal-tar creosote (P-13)[1]

Retention: Chromated copper arsenate	Retention: Creosote	Installation date	Present condition[2]	Total exposure	Exposure until average rating <6
———Pcf———				——— Years ———	
0.23	6.7	12/69	L	6-1/2	5-1/2
.23	13	12/69	L	9-1/2	8-1/2
.23	24	12/69	L	10-1/2	8-1/2
.59	5.2	12/69	L,E[3]	13	13
.59	18	12/69	2	13-1/2	12-1/2
.58	23	12/69	6	13-1/2	—
1.1	4.2	12/69	10	13-1/2	—
1.1	18	12/69	10	13-1/2	—
1.1	19	12/69	10	13-1/2	—
2.3	4.8	12/69	10	13-1/2	—
2.4	19	12/69	10	13-1/2	—
2.4	21	12/69	10	13-1/2	—

[1]Study supported in part by NFEC. FPL contact, B. R. Johnson.

[2]L, E = destroyed by *Limnoria*, microbial erosion.

[3]1 of 3 panels failed solely from microbial erosion.

Table 4-4.—Dual treatment with chromated copper arsenate (Type C) and English vertical-retort creosote[1]

Retention: Chromated copper arsenate	Retention: Creosote	Installation date	Present condition[2]	Total exposure	Exposure until average rating <6
———Pcf———				——— Years ———	
0.23	7.2	12/69	L	7-1/2	4
.23	16	12/69	L	10-1/2	9
.24	24	12/69	L	6-1/2	3
.60	7.6	12/69	L	11-1/2	9-1/2
.60	18	12/69	2	13-1/2	9-1/2
.60	23	12/69	L	10-1/2	9-1/2
1.1	9.2	12/69	6	13-1/2	—
1.1	13	12/69	2	13-1/2	12
1.1	27	12/69	4	13-1/2	12-1/2
2.6	9.4	12/69	10	13-1/2	—
2.6	13	12/69	10	13-1/2	—
2.3	18	12/69	10	13-1/2	—

[1]Study supported in part by NFEC. FPL contact, B. R. Johnson.

[2]L = destroyed by *Limnoria*.

Table 4-5.—Dual treatment with chromated copper arsenate (Type C) and land-grade coal-tar creosote (P-1)[1]

Retention: Chromated copper arsenate	Retention: Creosote	Installation date	Present condition[2]	Total exposure	Exposure until average rating <6
———Pcf———				——— Years ———	
0.24	5.7	12/69	L	5-1/2	5
.26	13	12/69	L	9	8-1/2
.24	16	12/69	L	11	8-1/2
.59	4.8	12/69	5	13-1/2	13-1/2
.59	17	12/69	6	13-1/2	—
.61	22	12/69	7	13-1/2	—
1.1	7	12/69	10	13-1/2	—
1.1	15	12/69	10	13-1/2	—
1.1	23	12/69	10	13-1/2	—
2.6	7.6	12/69	10	13-1/2	—
2.4	12	12/69	10	13-1/2	—
2.4	21	12/69	10	13-1/2	—

[1]Study supported in part by NFEC. FPL contact, B. R. Johnson.

[2]L = destroyed by *Limnoria*.

Table 4-6.—Dual treatment with chromated copper arsenate (Type C) and marine-grade coal-tar creosote (P-13)[1]

Retention: Chromated copper arsenate	Retention: Creosote	Installation date	Present condition[2]	Total exposure	Exposure until average rating <6
———Pcf———				——— Years ———	
0.24	5.2	12/69	L	7-1/2	6
.24	11	12/69	L	9	8-1/2
.23	19	12/69	L	13	9-1/2
.60	4.3	12/69	L,E	13	12
.60	16	12/69	2	13-1/2	12-1/2
.59	18	12/69	4	13-1/2	12-1/2
1.1	5.7	12/69	10	13-1/2	—
1.1	12	12/69	10	13-1/2	—
1.1	22	12/69	10	13-1/2	—
2.5	6.1	12/69	10	13-1/2	—
2.5	12	12/69	10	13-1/2	—
2.6	24	12/69	10	13-1/2	—

[1]Study supported in part by NFEC. FPL contact, B. R. Johnson.

[2]L, E = destroyed by *Limnoria*, microbial erosion.

Table 4-7.—Dual treatment with ammoniacal copper arsenate and English vertical-retort creosote[1]

Retention: Ammoniacal copper arsenate	Retention: Creosote	Installation date	Present condition[2]	Total exposure	Exposure until average rating <6
———Pcf———				——— Years ———	
0.26	8.3	12/69	L	9	6-1/2
.24	12	12/69	L	7-1/2	6-1/2
.24	26	12/69	L	9	7-1/2
.56	8.9	12/69	L,E	9-1/2	9-1/2
.57	12	12/69	L,T	8-1/2	7-1/2
.56	25	12/69	L	10-1/2	8-1/2
1.1	8.4	12/69	L,E[3]	12-1/2	11-1/2
1.1	12	12/69	E	13	—
1.1	23	12/69	L	13	11
2.2	8.2	12/69	9	13-1/2	—
2.3	11	12/69	10	13-1/2	—
2.2	27	12/69	10	13-1/2	—

[1]Study supported in part by NFEC. FPL contact, B. R. Johnson.

[2]L, T, E = destroyed by *Limnoria*, teredines, microbial erosion.

[3]1 of 3 panels failed solely from microbial erosion.

Table 4-8.—Dual treatment with ammoniacal copper arsenate and land-grade coal-tar creosote (P-1)[1]

Retention: Ammoniacal copper arsenate	Retention: Creosote	Installation date	Present condition[2]	Total exposure	Exposure until average rating <6
———Pcf———				——— Years ———	
0.22	5.4	12/69	L	7	5-1/2
.24	12	12/69	L	9	8
.23	21	12/69	1	13-1/2	8-1/2
.56	5.7	12/69	L	9	8
.58	14	12/69	L	12-1/2	9-1/2
.57	24	12/69	2	13-1/2	10
1.1	6.1	12/69	L,E[3]	11-1/2	11
1.1	12	12/69	8	13-1/2	—
1.1	26	12/69	7	13-1/2	—
2.3	6.1	12/69	7	13-1/2	—
2.3	13	12/69	10	13-1/2	—
2.4	25	12/69	10	13-1/2	—

[1]Study supported in part by NFEC. FPL contact, B. R. Johnson.

[2]L, E = destroyed by *Limnoria*, microbial erosion.

[3]1 of 4 panels failed solely from microbial erosion.

Table 4-9.—Dual treatment with ammoniacal copper arsenate and marine-grade coal-tar creosote (P-13)[1]

Retention: Ammoniacal copper arsenate	Retention: Creosote	Installation date	Present condition[2]	Total exposure	Exposure until average rating <6
———Pcf———				——— Years ———	
0.23	5.7	12/69	L	8	6
.23	12	12/69	L	8-1/2	7-1/2
.23	24	12/69	L	12	9
.57	6	12/69	L,E	11-1/2	9
.57	12	12/69	L	10-1/2	9
.57	23	12/69	L	12	9
1.1	6.4	12/69	10	13-1/2	—
1.1	13	12/69	2	13-1/2	12
1.1	24	12/69	10	13-1/2	—
2.4	5.9	12/69	10	13-1/2	—
2.4	13	12/69	10	13-1/2	—
2.4	25	12/69	10	13-1/2	—

[1]Study supported in part by NFEC. FPL contact, B. R. Johnson.

[2]L, E = destroyed by *Limnoria*, microbial erosion.

Table 4-10.—Dual treatment with ammoniacal copper borate and marine-grade coal-tar creosote (P-13)[1,2]

Retention: Ammoniacal copper arsenate	Retention: Creosote	Installation date	Present condition[3]	Total exposure	Exposure until average rating <6
———Pcf———				——— Years ———	
0.25	13	1/76	L	7-1/2	4-1/2
.60	12	1/76	7	7-1/2	—
1.2	15	1/76	10	7-1/2	—
2.5	13	1/76	10	7-1/2	—

[1]Study supported in part by NFEC. FPL contact, B. R. Johnson.

[2]15 replicates per treatment.

[3]L = destroyed by *Limnoria*.

Table 4-11.—Dual treatment with acid copper chromate and marine-grade coal-tar creosote (P-13)[1]

Retention: Acid copper chromate	Retention: Creosote	Installation date	Present condition	Total exposure	Exposure until average rating <6
———Pcf———				——— Years ———	
0.25	16	1/76	4	7-1/2	6
.60	16	1/76	10	7-1/2	—
1.2	16	1/76	10	7-1/2	—
2.8	16	1/76	10	7-1/2	—

[1]Study supported in part by Koppers Co. FPD. FPL contact, L. R. Gjovik.

Table 4-12.—Dual treatment with chromated copper fluoride and marine-grade coal-tar creosote (P-13)[1]

Retention: Chromated copper fluoride	Retention: Creosote	Installation date	Present condition	Total exposure	Exposure until average rating <6
———Pcf———				——— Years ———	
0.21	16	1/77	5	6	5-1/2
.57	19	1/77	8	6	—
1.1	21	1/77	10	6	—
2.3	19	1/77	10	6	—

[1]Study supported in part by Simonsen Chemical Co. FPL contact, L. R. Gjovik.

CHEMICAL MODIFICATION

Table 5.—Chemical modification[1]

Reagent	Weight gain	Installation date	Present condition	Total exposure	Exposure until average rating <6
	Pct			——— *Years* ———	
Butylene oxide	[2]23.7	12/77	10	5-1/2	—
	[3]28.5	6/78	10	5	—
Propylene oxide	[4]22.1	6/75	10	8	—
	[5]26.6	6/75	10	8	—
	[6]31.6	6/75	10	8	—
Butyl isocyanate and dimethylformamide	[2]29.3	7/80	10	3	—

[1]FPL contact, R. M. Rowell.

[2]10 replicates.

[3]12 replicates.

[4]3 replicates.

[5]5 replicates.

[6]2 replicates.

POLYMERS

Table 6-1.—Prepolymerized tributyltin methacrylate (TBTM) and methyl methacrylate (MeM) copolymers in organic solvents[1,2]

Solution formulation	Retention[3]	Installation date	Present condition	Total exposure	Exposure until average rating <6
	Pcf			*Years*	
TBTM/MeM in mineral spirits + P13 creosote	1.10 (polymer) 2.45 (creosote)	1/77	6	6-1/2	—
	0.97 (polymer) 2.16 (creosote)	1/77	7	6-1/2	—
TBTM/MeM in mineral spirits	13.9	1/77	10	6-1/2	—
	8.20	1/77	10	6-1/2	—
TBT ester of methyl vinyl ether/maleic anhydride, in cyclohexanone	6.20	1/77	10	6-1/2	—
	3.28	1/77	10	6-1/2	—
TBT oxide (2 pct) in mineral spirits	1.85	1/77	10	6-1/2	—

[1]Treatments devised and performed by David W. Taylor Naval Ship R&D Center. FPL contact, B. R. Johnson.

[2]Polymerization prior to impregnation of solution into wood. 6 replicates per treatment.

[3]Not including mineral spirits or cyclohexanone.

Table 6-2.—*In situ* polymerization of tributyltin-modified monomers[1,2,3]

Solution formulation	Retention	Instal-lation date	Present condition	Total exposure	Exposure until average rating <6
	Pcf			——— *Years* ———	
MeM	29.0	6/77	8	6	—
TBTM/MeM	22.8	6/77	10	6	—
TBTM/MeM with 1,3-butylene dimethacrylate	29.3	6/77	10	6	—
TBTM	35.0	6/77	10	6	—
	27.0	12/77	10	5-1/2	—
TBTM in mineral spirits	3.08 (polymer)	12/77	10	5-1/2	—
TBTM/GMA[4]	37.0	6/77	10	6	—
	23.6	6/77	10	6	—
	10.0	6/77	10	6	—
TBTM/epoxy, Type 1	6.22	6/77	10	6	—
TBTM/epoxy, Type 2	10.7	12/77	10	5-1/2	—
TBTM/MeM[5]	1.7	7/80	10	3	—
	0.8	7/80	10	3	—
	0.5	7/80	10	3	—
TBTM/GMA[5]	0.7	7/80	10	3	—

[1]Treatments devised and performed by David W. Taylor Naval Ship R&D Center, except as noted. FPL contact B. R. Johnson.

[2]6 replicates per treatment except as noted.

[3]MeM = methyl methacrylate; TBTM = tributyltin methacrylate; GMA = glycidal methacrylate.

[4]*4 replicates per treatment.* Treatments done by Washington State University for Taylor R&D Center.

[5]3 replicates per treatment.

Table 6-3.—*In situ* polymerization of modified methacrylate impregnants[1,2,3]

Solution formulation	Weight gain	Instal-lation date	Present condition	Total exposure	Exposure until average rating <6
	Pct			*Years*	*Years*
MeM	80.3	1/80	10	3-1/2	—
PCPM/MeM 1:4	80.5	1/80	10	3-1/2	—
1:8	83.5	1/80	10	3-1/2	—
1:16	81.3	1/80	10	3-1/2	—
TBTM/MeM 1:2	82.6	1/80	10	3-1/2	—
1:4	79.6	1/80	10	3-1/2	—
1:8	72.6	1/80	10	3-1/2	—
PBPM/MeM 1:8	82.7	1/80	10	3-1/2	—
1:16	87.1	1/80	8	3-1/2	—
1:32[4]	80.0	1/80	10	3-1/2	—

[1]FPL contact, R. M. Rowell.

[2]5 replicates per treatment except as noted. Note that retentions are percent weight gain, not pcf.

[3]MeM = methyl methacrylate; PCPM = pentachlorophenol methacrylate; TBTM = tributyltin methacrylate; PBPM = pentabromophenol methacrylate.

[4]10 replicates.

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PESTICIDE PRECAUTIONARY STATEMENT

This publication reports research involving pesticides. It does not contain recommendations for their use, nor does it imply that the uses discussed here have been registered. All uses of pesticides must be registered by appropriate State and/or Federal agencies before they can be recommended

CAUTION: Pesticides can be injurious to humans, domestic animals, desirable plants, and fish or other wildlife — if they are not handled or applied properly. Use all pesticides selectively and carefully. Follow recommended practices for the disposal of surplus pesticides and pesticide containers.

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